(NASA TM V- 51100)

X64 10931

N65-89014

Code 2A
ref Submitted for Publication

THE VISIBLE ABSORPTION SPECTRA OF CADMIUM IN CADMIUM HALIDES AND LEAD IN LEAD CHLORIDE AND IN LEAD BROMIDE

By J. Greenberg [1963]   9p

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio

ABSTRACT

10931

The visible band spectra for the cadmium - cadmium halide and the lead - lead halide systems have been observed. The relative positions of the band peaks of the cadmium - cadmium halides compared to those of the halides suggest that the species Cd_2^{++} is not formed but that the metal atom is situated in vacancies from which it contributes electrons to nearest cation neighbors.

AUTHOR

INTRODUCTION

An explanation of the solubility of neutral metal atoms in ionic liquids should account for the nature of the species in solution and indirectly the structure of the liquid. For this reason the visible and infrared absorption spectra of the cadmium - cadmium halides and lead - lead halides were obtained. It has been observed that new bands were formed when the metal is added to its salt. The peaks observed for these metal-salt systems occur at the same relative position to each other as do the peaks for the pure salts but at longer wavelengths. This is interpreted to mean that the absorption process in the metal-salt is relatively the same as in the pure salts but at lower energies.

The visible absorption process in the pure salts is a charge-transfer mechanism in which electrons are promoted from the anion to the nearest cation neighbors.[1] It would appear therefore that in the metal-salt systems, metal atoms are situated in vacancies and that their electrons are promoted into the energy levels of the salt in much the same manner as anion electrons in a "pure" salt. The solubility of these metals in their salts is therefore a function of the number of such vacancies present. If the salt is considered to have a quasi-lattice structure, then the vacancies to which the metal atoms accommodate themselves may be the type present in solids. That is, the vacancies are of the interstitial type and in addition, actual cation vacancies formed by the movement of the cation out of the quasi-lattice structure.

EXPERIMENTAL

Reagent grade materials were kept in a vacuum drying oven at 200° C for several days and then melted and filtered through Pyrex glass wool. The lead and cadmium metals had less than 1 percent impurity and were used without further purification.

Measurements in the visible were made using a model 13 Perkin-Elmer spectrophotometer equipped with a Nernst glower light source, fused silica prism and photomultiplier detector. The light source was phased by a chopper since the detector was susceptible only to an amplified a-c signal. This proved helpful in keeping the emission interference to a minimum since the black body radiation of the sample and cell were not phased. Investigations were also made in the infrared up to 15μ. For these measurements, the model 13 was equipped with a Nernst glower light source, NaCl prism and thermocouple detectors.

The platinum screen technique[2] was used to obtain data in the infrared. In order to prevent evaporation or oxidation of the samples on the platinum screen, the cell was kept under nitrogen pressure (~10psig) and the temperature of the sample was not allowed to reach more than $10°$ C above the melting point. The platinum screen cell was matched with air as a reference. This was done since the pure salts do not have an infrared absorption band to 15μ. The reference beam was attenuated to obtain the proper base line.

In the visible, the reference and sample cells were made from 8mm Pyrex tubing. These containers were then calibrated to form sets of cells with known differences in path length. In order to prevent air oxidation of the cadmium in the cadmium halide mixtures, the Pyrex containers were evacuated and sealed. No such precautions were necessary with the lead - lead halide systems. The cuvettes were heated by means of Nichrome ribbon, and the temperatures were controlled by means of an on-off relay to within $\pm2°$ C. The cells used in the visible were matched by adjusting the base-line of the instrument. It was therefore necessary to report the results as relative percent absorption. In order to isolate the absorption due to added metal from absorption due to the salt alone, the reference cell of the double-beam instrument was filled with the pure salt.

RESULTS

The data obtained are reported in table I and in figures 1 and 2.

TABLE I - VISIBLE ABSORPTION MAXIMA FOR CADMIUM

AND LEAD SALTS, AND METAL MIXTURES

Salt	$\lambda\mu$	$T(^{\circ}C)$
$Cd\ Cl_2$	0.360	588
$Cd\ Br_2$	0.500	600
$Cd\ I_2$	0.540	405
$Cd-Cd\ Cl_2{}^*$	0.455	573
	0.455	593
	0.45 - 0.55	618
$Cd-Cd\ Br_2{}^*$	0.605	605
$Cd-Cd\ I_2{}^*$	0.665	390, 410
$Pb\ Cl_2$	0.439	521
$Pb\ Br_2$	0.521	393
$Pb-Pb\ Cl_2$	0.627	550
$Pb-Pb\ Br_2{}^*$	0.692	450

*The absorption due to the pure salt is present
in addition to the maxima reported.

No specific infrared absorption bands were observed either in the pure salts or in the metal-salt mixtures. Decomposition of the lead iodide made it difficult to specify the spectra of the system, and these results were not reported. As in the case of the pure salts the effect of temperature on the metal salt bands was initially to broaden the band and then shift the peak position to lower energies (longer wavelengths). The splitting of the band, as observed in the case of

Cd in Cd Cl_2, a few degrees above the melting point is analogous to the splitting that occurs in the spectra of crystals when the absorbing species can have more than one orientation in the lattice. A possible explanation of this effect may be due to the fact that the metal atom can occupy either an interstitial vacancy or a hole formed by the displacement of a cation. As the temperature is raised, the band broadens and the split is not seen.

DISCUSSION

It appears that two types of solutions are formed upon the addition of a metal to its salt. In the case of the alkali, alkaline earth, or the rare-earth systems electronically conducting solutions are formed. However, systems such as Cd, Pb, Bi - halide mixtures remain electrolytic conductors. The mechanism whereby electronic conduction appears has been attributed to the dissociation of the metal atom into a cation and an electron.[3] The resulting electrons then have sufficient energy to move in the conduction band. Essentially two explanations have been given for the case where electrolytic conduction prevails. A solution is formed upon the addition of the metal whereby the metal atoms occupy holes in the quasi-lattice formed by the halide ions.[4] The other explanation for the case of electrolytic conduction indicates that the metal atoms react with the cations to form a subhalide. Since Cd^+ would not be diamagnetic, the presence of this species was discounted by magnetic susceptibility measurements.[5]

The presence of specific bands in the case of the cadmium and lead metal-salt systems indicates that the metal as present in the salt does

not possess close-spaced electronic levels characteristic of the metal in the pure state. The presence of such levels would result in a continuum in the visible spectral region. This has been confirmed by the diamagnetic behavior of the cadmium metal-salt system since "metallic" behavior is characterized by a paramagnetic effect.[6]

The fact that these bands do not overlap or center about some mean position indicates that the electronic transition involved is not primarily concerned with an individual ion. In other words, if Cd_2^{++} were specifically formed in the cadmium - cadmium halide systems by a reaction between the cadmium metal atom and cadmium cation, i.e., $Cd + Cd^{++} = Cd_2^{++}$, the visible spectral bands would appear at relatively the same place since the electronic transition would only be slightly influenced by the presence of the anions.

What is observed, however, is that the unique bands for the metal-salt systems have the same relative positions to each other as do the pure salts. This would be seen even more clearly if account is taken of the temperature influence on the position of the band peak as well as the fact that the peak position for the pure molten salts is estimated.[1] The fact that the metal-salt systems have unique bands with the same relative position to each other as the salts themselves suggests that the energy level structure for the metal-salt system is similar to that of the salts but that the initial electron transfer process occurs at lower energies. In other words, the metal atoms contribute electrons to the established energy levels in the salt. It is possible therefore to consider the electron transfer to occur not

between metal atoms and dissociated mobile cations which would lead to the formation of Cd_2^{++}, but that the electron transfer process occurs between metal atoms and the undissociated or quasi-lattice portion of the salt. In this case the electron would be promoted from the metal atom situated in a vacancy to the nearest cation neighbors in the quasi-lattice. The charge distribution of the cation neighbors in this case would be modified by the presence of the anions and account for the separate bands observed when the metal is added to its halide salts. This electron transfer process has been used to explain the enhanced diamagnetism in the cadmium - cadmium chloride solution.[6] That this electron transfer would be of low energy is suggested by the fact that it takes less energy to ionize a metal in an ionic medium than in vacuum.[7]

The visible absorption process for the metal-salt systems is analogous to the absorption process in pure salts. The process of visible absorption in ionic salt systems has been attributed to the electronic charge transfer from the anion to the nearest cation neighbors. This results in the formation of an exciton. The components of the exciton are a halogen atom and an electron moving in expanded orbits of nearest cation neighbors. In accordance with the suggestion that the metal-salt systems have an initial low energy electron transfer with the same energy level structure as the salt, the metal atoms may contribute electrons to expanded orbits involving nearest cation neighbors in the quasi-lattice structure of the melt. The results of this charge transfer are a cation and an electron moving in an expanded orbit.

The mechanism for both electronic and electrolytic metal-salt solutions would therefore involve the accommodation of the metal atom to the number of vacancies present. In the case of electronically conducting systems, the electron can be considered to be delocalized. This mechanism helps to explain the selective solubility of metals in salts. That is, the salt functions as a membrane which can dissolve only particular metal atoms.

It is of interest to note that the exciton phenomena in "pure" salts can be used to explain the stability of these systems upon melting. In the halides the charge transfer process results in the formation of a halogen atom. For the iodide systems this is a relatively low energy process and decomposition of the system upon melting is observed. It may be that such decomposition occurs upon melting to varying degrees in all ionic halide systems and may be responsible for the residual emf's observed in electrical conductance measurements and in the determination of Seebeck coefficients.

REFERENCES

1. B. R. Sundheim and J. Greenberg, J. Chem. Phys. 28 439 (1958).

2. J. Greenberg and L. Hallgren, J. Chem. Phys. 33 900 (1960).

3. H. R. Bronstein and M. A. Bredig, J. Am. Chem. Soc. 80 2077 (1958).

4. D. Cubic021oti, J. Metals 5, AIME Trans. 197 1106 (1953).

5. K. Grjotheim, F. Gronwald, and J. Krogh Moe, JACS 80 2077 (1958).

6. N. H. Nachtrieb, J. Phys. Chem. 66 1163 (1962).

7. N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Clarendon Press, Oxford, England, 2nd ed. (1948).
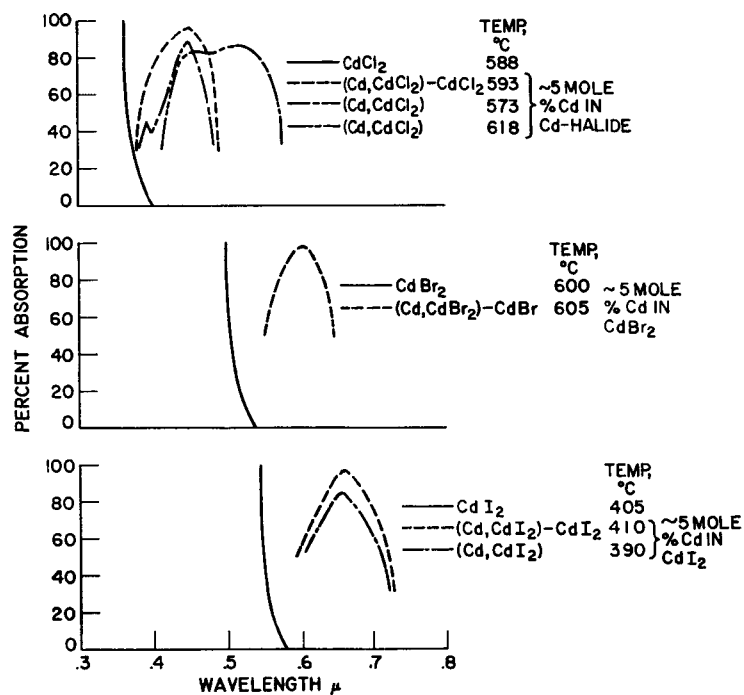
Figure 1. - Visible absorption spectra of cadmium halides and cadmium in cadmium halides.
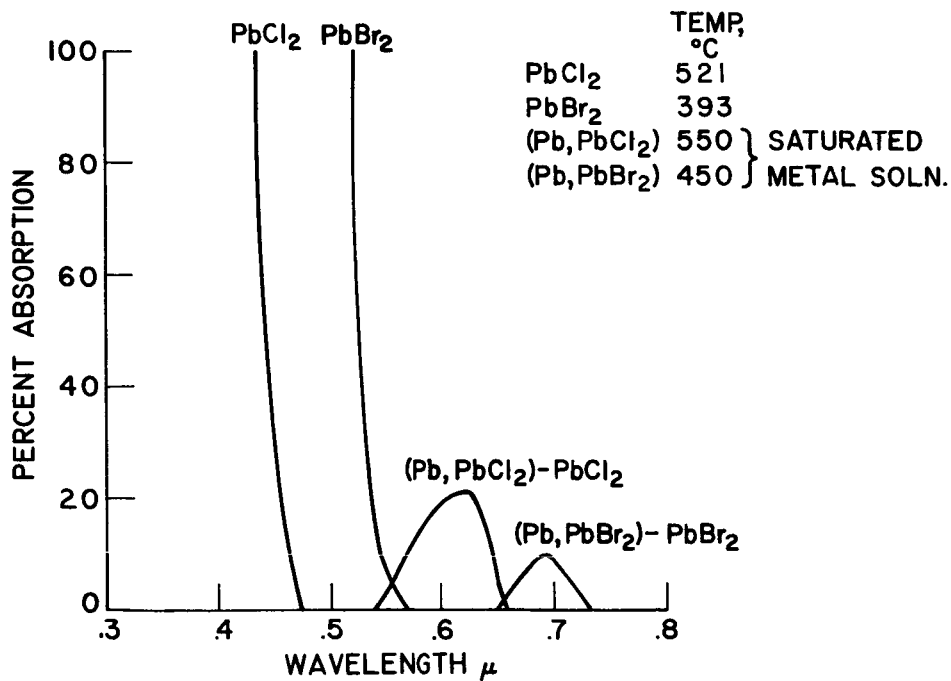

Figure 2. - Visible absorption spectra of PbCl$_2$, PbBr$_2$ and Pb in PbCl$_2$, PbBr$_2$.